

PATENT SPECIFICATION

NO DRAWINGS

1.004.333

1.004.333



Date of Application and filing Complete Specification March 29, 1962.

No. 12082/62.

Application made in United States of America (No. 99,726) on March 31, 1961.

Complete Specification Published Sept. 15, 1965.

© Crown Copyright 1965.

Index at acceptance:—G2 C(A4, C10A1, C10A3, C10AX, C10B, C10D, C10X)

Int. Cl.:—G 03 c

COMPLETE SPECIFICATION

Improvements in and relating to Photographic Processing

We, EASTMAN KODAK COMPANY, a Company organised under the laws of the State of New Jersey, United States of America, of 343 State Street, Rochester 4, New York, United States of America (Assignees of JOHN CARLETON BARNES and EDWIN BERTON WYAND) do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the processing of photographic materials.

According to the present invention there is provided a method of processing an exposed photographic silver halide emulsion layer so as to form a silver image therein or so as to tone, bleach or fix a silver image in the layer which comprises incorporating in the appropriate, alkaline, processing liquid a gum mucilage which thickens the liquid and which will react with borate ions when introduced into the liquid to cause the liquid to set, forming a layer of the processing liquid containing the gum mucilage, contacting this layer with the emulsion layer and allowing the processing reaction to take place, introducing into the liquid before or after forming the layer thereof said borate ions and removing the set layer of processing liquid from the emulsion layer after the processing reaction has taken place.

When processing is complete the set composition together with the by-products of the processing can be removed in a more or less coherent mass leaving a processed material which requires little, if any, washing.

The gum mucilages employed in this invention have a thickening effect on some processing liquids when dissolved therein the thickened liquids have a viscosity substantially greater than water. In addition to the gum mucilage an auxiliary thickening agent such

as gelatin or carboxymethyl cellulose may be present in the processing liquid.

According to one form of the present invention the viscous photographic processing liquid containing the gum mucilage is coated on an exposed photographic emulsion layer and then contacted with borate ion so that the processing liquid is "set" almost immediately thus preventing slipping of the processing layer relative to the emulsion layer while at the same time permitting optimum photographic processing to continue without apparent chemical impedance to produce a photographic result of optimum quality. After the time required for processing, the "set" or gelled processing layer can then be removed by simply spraying with water or stripping.

The gum mucilages which are employed in this invention and which are "set" on contact with borate ion, are compounds which have available cis-hydroxy groups. These gum mucilages include, for example, guar gum, locust bean gum, locust kernal gum, damson gum, psyllium gum, cherry gum, slippery elm gum (*Alnus fulva*), Salep mannan, mannans from orchis morio, galactomannans from *Trigonella foenum groccum*, alginates (e.g. monoglycol ester of alginic acid), the endosperm of *Cerantonia siligua*, gum ghatti, linseed gum, flaxseed gum and gum arabic.

Typical locust bean gums comprise carob gum, gum Hevo, gum Gatto, Jandagum, Lupogum, Luposol, Rubigum and Tragasol.

The processing liquids in which are incorporated the gum mucilages for use according to the invention comprise devolping solutions, fixing solutions or combined developing and fixing solutions.

The amount of gum mucilage added to such solutions can vary widely. Usually from 0.1% to 5% by weight of the total weight of the solution is suitable, with preferred concentra-

tions ranging from 0.5% to 2.5% of the total weight of the processing solution.

The gum mucilages used in the present invention are readily soluble in any of the processing solutions described herein. The combined developing and fixing baths can be prepared conveniently as needed by dissolving the dry chemicals of the processing bath in the appropriate volume of water after which the gum mucilage can conveniently be dissolved therein.

When in the present specification and appended claims we use the term borate ion, we mean the ion:

15



The compounds used in our invention to provide the boration can thus contain this ion per se, or can react with water, or one of the ingredients in the processing bath, to produce this ion.

The compounds which can be employed to set the process liquid comprise boric acid itself (H_3BO_3), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and alkali metal metaborates. Also perborates (eg $\text{NaBO}_3 \cdot \text{H}_2\text{O}$) and alkali metal pyroborates or tetraborates may be used.

There are a number of ways in which the method of the present invention can be practised. According to one method the compound providing boration is incorporated in the emulsion layer to be processed prior to processing. According to this method when the layer of processing liquid containing the gum mucilage is applied to the emulsion layer the borate ion diffuses to the processing layer causing the processing solution to be gelled or "set". The gelled coating thereafter remains closely adherent to the emulsion layer so that substantially no "slippage" or spreading occurs between the emulsion layer and the "set" processing layer. The layer can be removed when processing is complete by any convenient means such as stripping. Ordinarily water is not needed in removing the gelled layer and for that matter subsequent treatment is usually not required to complete the process. Another method of removing the set layer comprises placing a piece or strand of absorbent paper such as KODAK 'Verifax' copy paper, over a coated processing or processed emulsion layer without pressure. The moist, gelled processing layer partially absorbs in to the overlay paper so that upon removal of the paper after allowing sufficient time for processing, the gelled processing layer completely adheres to the paper and is thereby removed, leaving a clean, developed emulsion layer. (KODAK and 'Verifax' are registered trade marks).

In another method of the invention, borate ion is not incorporated in the photographic emulsion layer to be processed, but is incorporated into the absorbent overlay paper. In

this instance the viscous, thickened processing solution is coated upon the exposed film and the absorbent paper containing the borate ion is immediately brought into contact with the uppermost surface of the processing layer and maintained in contact until processing is complete. Diffusion of borate ion from the paper into the layer causes gelation of the solution between the emulsion and the paper, and after processing, the gelled layer can be stripped away by merely removing the paper.

Both of these procedures offer important advantages with respect to processes involving the surface application of processing solutions such as monobaths. Since washing is not required to remove the layer, the process can be conducted in the absence of a supply of water, and equipment can therefore be made portable and greatly simplified. Since the solution is gelled after coating, the initial viscosity of the solution can be considerably lower than when gelation is not accomplished, and this makes possible the use of much simpler coating techniques. If, for example, the coating is such that gelation does not occur, the viscosity of such coatings must be so high that great difficulty is often encountered in feeding the solution to the emulsion layer by means of gravity. If, however, the solution is rapidly gelled as in the present invention, it is possible to use solutions of sufficiently low viscosity as to make gravity feed applications very simple and practical. In addition, the application of the absorbent overlay paper increases the stability of the viscous coating so that it can be more easily handled and passed by mechanical stations without damage.

In the present invention the gelling thickener can be employed in any single solutions of developers, bleaches, fixers, toners and hardeners or combinations thereof which may be of photographic interest provided alkaline conditions can be tolerated. Of particular interest in the present invention is the use of the gelling thickener in monobath processing solutions and such solutions containing development nuclei. Suitable combined developing and fixing solutions have been described in U.S.Ps. 2,782,120 and 2,782,121. Any well-known photographic developing agent can be employed in the combined developing and fixing solution. Suitable developing agents include N-monomethyl-p-amino-phenol sulphate dihydroxybenzene, dihydroxy-naphthalene; hydroquinone compounds, e.g. chlorohydroquinone, dichlorohydroquinone, bromohydroquinone and dibromohydroquinone; p-phenylene diamines, e.g. N,N-di(hydroxy-ethyl)-para-phenylene diamine, N-β-methane-sulphonamidoethyl-4-aminoaniline and N-β-sulphoamidoethyl-4-aminoaniline; 1-phenyl-3-pyrazolidone and its derivatives; and triaminophenols, including 2,4,6-triaminophenol, catechol, pyrogallol and ene-diols.

Suitable 1-phenyl-3-pyrazolidone developing agents include 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-p-aminophenyl-4-methyl-4-propyl-3-pyrazolidone and 1-p-chlorophenyl-4-methyl-4-ethyl-3-pyrazolidone. Especially useful developing compositions comprise mixtures of N-monomethyl-p-aminophenol sulphate and hydroquinone 1-phenyl-3-pyrazolidone and hydroquinone and 4,4-dimethyl-1-phenyl-3-pyrazolidone and hydroquinone. Other suitable 3-pyrazolidone developing agents and methods for preparing the pyrazolidone compounds herein disclosed can be prepared according to the disclosure in U.K. Specification 757271.

In those combined developer and fixing baths which contain a gum mucilage for use in the present invention and which contain nucleating agents for physical development these nucleating agents can include colloidal metals, e.g. colloidal silver or colloidal gold; colloidal metal sulphides, e.g. of zinc, lead, chromium, gallium, iron, cadmium, cobalt, nickel, silver or copper and certain metal selenides, e.g. of lead, zinc, antimony and nickel. Suitable nucleating agents for use in the invention are disclosed in U.S.P. 2,698,236. The amount of the nucleating agent in the combined developing and fixing solution is not critical. It was found that very small amounts of the nucleating agents gave favourable results in the processed film, and that very high concentrations of nucleating agent in the processing solution did not give unfavourable results. It was determined, however, that the presence of nucleating agents in the range from 0.1 gram per litre to 5.0 grams per litre were suitable. The range of concentration accordingly varies to some extent depending upon the nucleating agent employed.

It was found also that the concentrations of other ingredients in the combined developing and fixing baths used in the present invention can be varied in the general known manner within wide limits in order to produce gammas ranging from as low as 0.3 to as high as 1.4 in order to suit the intended application. As in conventional processing the inherent characteristics of the photographic film or plate partially determine the gamma obtained with any formula. It was apparent with any of the combined developing and fixing baths used in the practice of the invention that the gum mucilage in no way interfered with the natural progress of processing. By balancing both the concentration of the gum mucilage in the processing solution and the borate compound in the emulsion layer or in the absorbent paper laid over the top of the processing layer, the original viscosity and the rate of gelling could be adjusted to optimum values.

Photographic processing compositions, for example, monobaths, can also be successfully

employed in the surface layer processing of photographic materials according to the invention where a film-forming additive, such as polyvinyl alcohol, cellulose ether phthalate or a copolymer of acrylic acid and ethyl acrylate, is incorporated in the liquid. In such cases heat can be applied to a surface layer of the processing liquid to promote drying of the composition and formation of a film which can be then readily removed, for example, by stripping, when processing is complete.

The processing time normally required in the method of the invention is 1 to 10 minutes at 70° F. dependent to some extent, of course, upon the speed and type of negative films employed. In each case the above compositions resulted in developed and fixed silver images of good quality.

The following are examples of some of the ways in which the method of the present invention can be carried out. (Percentages are by weight).

EXAMPLE 1

This Example illustrates processing a well-known silver chloro-bromide photographic film using a combined developing and fixing solution containing guar gum and a borate-impregnated overlay pad.

The exposed photographic film was coated at a thickness of 0.01 inch with a monobath of the following composition:

TABLE 1

Sodium carbonate (anhydrous)	40.0 g.	
1-phenyl-4,4-dimethyl-3-pyrazolidone	0.4 g.	100
Hydroquinone	11.0 g.	
Potassium iodide	0.5 g.	
Sodium thiosulphate	16.0 g.	
Gum Jaguar (guar gum)	1.0 g.	105
Colloidal silver	0.39 g.	
Water to make	1.0 litre	

A strip of unsized white paper impregnated with sodium tetraborate was placed over the Gum Jaguar thickened monobath layer. After approximately 3 to 4 minutes processing time, the paper was separated from the film removing the entire processing strata, leaving a clean negative image only slightly moist. The negative image produced was of excellent quality.

The Gum Jaguar was purchased from Stein-Hall, Inc. Murray Hill Building, New York 17, N.Y.

EXAMPLE 2

This Example illustrates impregnating the negative film directly with boric acid.

A sample of exposed 'Recordak' Microfile film was treated by soaking in a 2% solution of boric acid for two minutes after which the film was dried. A viscous monobath of

the composition shown in Table 1 was coated upon the treated film after exposure and was allowed to remain for five minutes, whereupon a sheet of unsized white paper was laid on the surface of the viscous layer and then stripped off removing the viscous layer. This treatment resulted in a satisfactorily developed and fixed image and the emulsion surface after removal of the viscous processing layer was completely free of viscous residue and was only slightly damp. 'Recordak' is a registered trade mark.

EXAMPLE 3

This Example illustrates a modification of the invention wherein the guar gum-containing monobath is applied to a sodium metaborate-containing processing web whereupon the modified web is contacted with a negative film to be processed.

A processing web was prepared as follows: A 7% gelatin solution containing colloidal silver was coated on a subbed-cellulose acetate support at a thickness to give 1.5 grams of gelatin and 6 mg. of colloidal silver per square foot. The coating solution as prepared also contained a hardening agent, such as those described in U.S.Ps. 2,725,294 and 2,725,295 and a dispersing agent, such as those described in U.S.P. 2,379,373. The processing web was prepared by coating the gelatin composition in a manner similar to that in which gelatin silver halide emulsions are coated. After drying the processing web which comprised a gelatin pad was soaked for 2 minutes at 70° F. in a 2% sodium metaborate solution. After soaking, the processing web was dried.

The processing step was carried out as follows:

The processing web prepared as in the paragraph above was overcoated at a thickness of 0.01 inch with a guar gum-containing processing solution of the following composition:

TABLE 2

2 - dimethylaminoethanol-SO ₂ addition product (30% SO ₂ by weight)	100.0	g.
2 - dimethylaminoethanol	74.0	g.
1 - phenyl - 4,4 - dimethyl-3-pyrazolidone	1.0	g.
Hydroquinone	10.0	g.
Gum Jaguar (A-20A)	12.5	g.
Sodium thiosulphate	8.0	g.
Water to make	1.0	litre

The processing web having an overcoating of the above composition was rolled in contact with an exposed silver chlorobromide negative film. After remaining in contact for approximately 3 minutes, the processing web was separated from the exposed negative film and a developed and fixed negative image of excellent quality was obtained.

In the processing web as illustrated by this Example any of the well-known hydrophilic organic colloids can be used in place of gelatin. Suitable colloids comprise polyvinyl alcohol, cellulose derivatives and mixtures of hydrophilic colloids and hydrosols as described in U.S.P. 2,772,166.

EXAMPLE 4

This Example illustrates a modification of the invention wherein physical development nuclei are incorporated into the viscous monobath. The method of processing according to this example was the same as that used in Example 3 except that the following gum mucilage containing viscous monobath was employed:

TABLE 3

Sodium carbonate (anhydrous)	40	g.	80
Hydroquinone	11.0	g.	
1 - phenyl - 4,4 - dimethyl-3-pyrazolidone	1.0	g.	
Sodium thiosulphate	8.0	g.	
Potassium iodide	0.4	g.	85
Monoglycol ester of alginic acid	20.0	g.	
1 N sodium sulphide	6.0	cc.	
1 N silver nitrate	6.0	cc.	
Naphthalene sulphonie acid	10.0	cc.	90
Water to make	1.0	litre	

The processing time for this Example was 10 minutes at 70° F. after which the processing web and the negative film were separated and a developed and fixed negative of excellent quality was obtained.

EXAMPLE 5

In this Example an exposed chlorobromide negative film was soaked for 1 minute at 68° F. in a 2% boric acid solution after which the negative was overcoated at a thickness of 0.02 inch with a processing solution of the following composition:

TABLE 4

Sodium carbonate (anhydrous)	40.0	g.	105
Hydroquinone	11.0	g.	
Phenidone developing agent	2.0	g.	
Sodium thiosulphate	8.0	g.	
Potassium iodide	0.4	g.	
Locust bean gum	10.0	g.	110
Naphthalene sulphonie acid	10.0	cc.	
Water to make	1.0	litre	

The negative film overcoated with a composition as shown in the above Table was allowed to process for 10 minutes at 70° F. The processed negative was then sprayed with cold water to wash off the processing solution. On viewing a developed and fixed negative image of good quality was observed.

Any of the above described processing methods wherein a boric acid compound is

impregnated either in the negative photographic film or in an absorbent overlay paper, various monobath processing solutions containing a gum mucilage can be employed. For example, where it is desired to process high and medium speed panchromatic and orthochromatic roll films, surface layer processing solutions of the following compositions can be employed:

TABLE 5

10	Sodium sulphite (anhydrous)	50.0	g.
	Diaminophenol hydrochloride	15.0	g.
	Hydroquinone - - - -	5.0	g.
	Glycine - - - -	10.0	g.
15	6-nitrobenzimidazole nitrate, 0.5% solution - - - -	80.0	cc.
	Potassium bromide - - - -	5.0	g.
	Sodium hydroxide - - - -	20.0	g.
	Ammonium thiosulphate - - - -	50.0	g.
20	Gum arabic - - - -	25.0	g.
	Water to make - - - -	1.0	litre

The approximate time for processing using the above composition was 3 to 4 minutes at 68° F resulting in good gamma in high speed panchromatic films.

Another processing solution suitable for use in the present invention comprises a composition such as the following:

TABLE 6

30	Sodium sulphite (anhydrous)	30.0	g.
	Hydroquinone - - - -	15.0	g.
	Sodium thiosulphate - - - -	8.0	g.
	Sodium hydroxide - - - -	28.5	g.
	Cherry gum - - - -	18.0	g.
35	1 N sodium sulphite - - - -	3.0	cc.
	1 N silver nitrate - - - -	3.0	cc.
	Naphthalene sulphonie acid - - - -	20.0	cc.
	Water to make - - - -	1.0	litre

In the composition of Table 6 optimum photographic results can be obtained where other gelling thickeners are used, e.g. psyllium gum, e.g. at 20 grams per litre, flaxseed gum, e.g. at 15 grams per litre and linseed gum, e.g. at 18 grams per litre.

It was found that any of the processing solutions as disclosed in any of the above formulæ could be readily prepared without any difficulty in respect to the solubility of the ingredients.

As is known in the art, photographic processing solutions undergo changes in composition and therefore changes in activity with use. As more and more film is processed with a given amount of a developer solution, these changes become significant and ultimately produce unsatisfactorily developed films. Usually these changes are such that the developer becomes weaker, or less capable of developing sufficient density in the film at a given time of development. To overcome these difficulties, it has been proposed in the

art to replenish developer solutions by various means as well as to design developer tanks in such a way as to minimise aerial oxidation. The present invention overcomes these disadvantages by natural means since the silver halide emulsion layer to be processed contacts only fresh processing liquids, and the surface layer can be applied sufficiently thin to substantially reduce the over-all cost of materials employed in a processing operation.

Another advantage of the form of the present invention wherein a developer-fixer solution is used is the time saved by combining the developing and fixing steps into a single time-minimised step which requires only a minimal washing and in some cases no washing at all. Further advantages are realised in the case with which the method of the present invention can be practised and the fact that elaborate processing equipment is not needed in carrying out the process. By "setting" the surface processing layer on the film surface to be processed, low viscosity solutions can be used which are readily and uniformly applied to the film surface. Subsequently the "set" layer is readily and completely removable by washing and by methods herein described.

WHAT WE CLAIM IS:—

1. A method of processing an exposed photographic silver halide emulsion layer so as to from a silver image therein or so as to tone, bleach or fix a silver image in the layer which comprises incorporating in the appropriate, alkaline, processing liquid a gum mucilage which thickens the liquid and which will react with borate ions when introduced into the liquid to cause the liquid to set, forming a layer of the processing liquid containing the gum mucilage, contacting this layer with the emulsion layer and allowing the processing reaction to take place, introducing into the liquid before or after forming the layer thereof said borate ions and removing the set layer of processing liquid from the emulsion layer after the processing reaction has taken place.

2. A method according to claim 1 in which the gum mucilage is guar gum, locust bean gum, gum arabic, cherry gum, a monoglycol ester of alginic acid, psyllium gum, flax seed gum or linseed gum.

3. A method according to claim 1 or 2 in which the liquid contains from 0.5% to 2.5% by weight of the gum mucilage, based on the total weight of the liquid.

4. A method according to claim 1, 2 or 3 in which the emulsion layer contains boric acid and said borate ions are introduced into the layer of processing liquid by diffusion of the boric acid thereinto.

5. A method according to any of claims 1 to 3 in which the borate ions are introduced into the layer of processing liquid on the

emulsion layer by contacting the layer with a web or sheet carrying a water-soluble borate which forms the borate ions on diffusion into the layer of processing liquid.

5 6. A method according to claim 5 in which the web is such that the set processing liquid adheres thereto.

7. A method according to claim 6 in which the web or sheet is an unsized paper web or sheet.

10 8. A method according to any of claims 1 to 3 in which the borate ions are introduced into the layer of processing liquid containing the gum mucilage before said contacting by first coating the layer of processing liquid containing the gum mucilage on a web or sheet carrying a water-soluble borate which forms the borate ions on diffusion into the processing liquid.

15 9. A method according to any of claims 1 to 8 in which the processing liquid is a combined developing and fixing liquid.

10. A method according to claims 8 and 9 in which the fixing agent comprises physical development nuclei and a silver halide solvent.

25 11. A method according to claim 10 in which the borate ions are introduced into the combined developing and fixing liquid containing the gum mucilage by coating the liquid on a hydrophilic colloid layer which has been impregnated with a water-soluble borate which forms the borate ions on diffu-

sion into the processing liquid and which is on a support.

12. A method according to claim 8 in which the processing liquid is a developing liquid containing a silver halide solvent and the gum mucilage and is coated on a layer of a hydrophilic colloid containing physical development nuclei which has been impregnated with a water-soluble borate which forms the borate ions on diffusion into the processing liquid and which is on a support, the silver halide solvent and the nuclei together acting at fixing agents.

13. A method according to any of claims 9 to 12 in which the developing agent is hydroquinone and a 1-phenyl-3-pyrazolidone or hydroquinone and an N-alkyl-p-amino phenol acid salt.

14. A method according to claim 10, 11 or 12 in which the nuclei are colloidal silver or silver sulphide particles and the solvent is sodium thiosulphate.

15. A method of developing and fixing an exposed photographic film substantially as described in any of Examples 1 to 5.

16. A photographic material comprising a photographic silver halide emulsion layer prepared by a method according to any of the preceding claims.

L. E. T. BRANCH, B.Sc., F.R.I.C.
Patent Agent.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1965.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.